PHYSICAL REVIEW B VOLUME 13, NUMBER 8 15 APRIL 1976

Unrestricted-Hartree-Fock approach to cluster calculations: Application to lithium*

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(Received 6 October 1975)

In this paper, we examine theoretical techniques for studying clusters of atoms. We examine the traditional restricted-Hartree-Fock method, the general-valence-bond method, and the space-spin unrestricted-Hartree-Fock method. We perform a series of calculations to determine the structure of fine particles of lithium and conclude that the most accurate available simple Hartree-Fock-type method is the unrestricted-Hartree-Fock method. These results are contrasted to recent studies on similar systems employing the self-consistent field $X\alpha$ scattered-wave approach, and we conclude on the basis of inferences from experimental data that the unrestricted-Hartree-Fock method produces results in fair agreement with the $X\alpha$ method for such metal systems, and that important differences exist between both methods.

I. INTRODUCTION

In the past several years, cluster approximations have proven successful in solving problems of interest in the areas of solid-state and surface physics.[1-5] By the cluster approximation, we mean that a large solid system is approximated by a finite group of atoms or ions which may in turn be placed in a field to simulate the remainder of the solid. More recently, cluster methods have been employed because small clusters are of interest in themselves, rather than merely a representation of a larger system.[1,5,6] Small clusters are of great current importance in that they may realistically represent systems of use for homogeneous catalysis or the active site (usually groups of 6-12 transition-metal atoms) used on a silica or alumina-supported industrial catalyst.[7] In addition such small systems may represent some of the radiation-damage products occurring in materials subjected to intense radiation.[8]

In this article we attempt two things. The first is a systematic critique of methods to be used for cluster calculations, and the second is a study of fine particles of metallic Li. We conclude that the unrestricted-Hartree-Fock (UHF) method or perhaps a semi-empirical derivative of it would be an adequate model for such a system. We further argue on the basis of a comparison of results from the present calculation with those of the self-consistent-field $X\alpha$ scattered-wave approach,[1,5,6] and with inferences from experimental data, that the UHF method may be in better agreement with experiment than is the $X\alpha$ result.

In Sec. II, we discuss the salient features of the various theoretical methods available for cluster studies and draw some preliminary conclusions. In Sec. III, we discuss the specific calculations performed on the Li cluster, and finally in Sec. IV we discuss the experimental situations and arrive at our conclusions.

II. THEORETICAL METHODS

We begin the theoretical discussion by a general discussion of the Hartree-Fock technique. We assume the usual nonrelativistic Hamiltonian

$$\mathcal{H} = -\sum_{i=1}^{n} \frac{\hbar^2}{2m} \nabla_i^2 - \sum_{i,I}^{n,N} \frac{e^2 Z_I}{|\vec{r}_i - \vec{R}_I|} + \sum_{i>j=1}^{n} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} . \tag{1}$$

In Eq. (1), upper case letters refer to nuclear to coordinates, with Z_I being the charge on the Ith nucleus, and $\vec{R}_I$ its position. Lower case letters refer to electronic coordinates. The mass of the electron is m and e is the electron charge. In this article we adopt atomic units, so that $e = m = \hbar = 1$. The unit of energy is the Hartree (1 Hartree ≈ 27.2 eV), the unit of length in a.u. is the hydrogen-atom bohr radius (1 a.u. = 1 bohr radius ≈ 0.53 Å). We assume that we may approximate the eigenstates of $\mathcal{H}$ given by Eq. (1) by a single Slater determinant of one-electron eigenfunctions so that

$$\Psi(\vec{r}_1 \cdots \vec{r}_n) = (n\,!)^{-1/2} \tilde{A}[\varphi_1(\vec{r}_1)\,\alpha\varphi_2(\vec{r}_2)\,\alpha \cdots \times \varphi_j(\vec{r}_j)\,\alpha\varphi_{j+1}(\vec{r}_{j+1})\,\beta \cdots \varphi_n(\vec{r}_n)\,\beta] . \tag{2}$$

In Eq. (2) we assume n electrons in the system of which j have spin up and $n-j$ spin down. $\tilde{A}$ is the antisymmetrizing operator and α is the spin-up spin eigenfunction and β is the spin-down eigenfunction. If one requires that

$$\int \varphi_a(\vec{x})\,\varphi_b(\vec{x})\,d\vec{x} = \delta_{ab} , \tag{3}$$

when $\vec{x}$ includes both space and spin coordinates of the orbital, and if one requires the expectation value of $\mathcal{H}$ to be minimized for the orbitals of Eq. (2), one has the equation for the φ's occurring in (2) of the form

$$F\varphi_a = \epsilon_a \varphi_a = \left(-\tfrac{1}{2}\nabla^2 - \sum_{I=1}^{N} \frac{Z_I}{|\vec{r} - \vec{R}_I|} + \int \frac{\rho(\vec{x}', \vec{x}')}{|\vec{r} - \vec{r}'|}\, d\vec{x}' \right.$$

$$-\frac{\rho(\vec{x},\vec{x}')P(\vec{x},\vec{x}')}{|\vec{r}-\vec{r}'|}\Bigg]\varphi_a(\vec{x}) . \tag{4}$$

Here one has

$$\rho(\vec{x},\vec{x}')=\sum_{i=1}^{n}\varphi_i(\vec{x})\varphi_i^\dagger(\vec{x}') , \tag{5}$$

and $P(\vec{x}, \vec{x}')$ is the operator which interchanges coordinates $\vec{x}$ and $\vec{x}'$.

If Eq. (4) is solved in its full generality for the $\varphi_a(\vec{x})$ with no further assumptions or constraints being placed upon the $\varphi_a(\vec{x})$, we term this equation the unrestricted-Hartree-Fock equation (UHF). Löwdin has devoted much effort to discussing the effects of adding constraints to this equation and the potential for degrading the quality of the resulting variational energy due to such constraints.[9] We shall here consider only the effects of two such constraints and refer the interested reader to the article by Löwdin for further detail. We do, however, note two substantial advantages to the unrestricted form of the Hartree-Fock theory. The first advantage is that chemical bonds dissociate properly, an advantage shared with the $X\alpha$ local-density energy-functional method. The second advantage is that electrons of opposite spin may begin to avoid each other on the average. That is, electrons of opposite spin may correlate. In fact, for the case of a free-electron gas, the UHF solutions tend to appear like a Wigner lattice.[10,11]

The simplest level of additional constraint which one may employ is to require that the spin-up, spin-down solutions be different but that the spatial part of each orbital be a symmetry-adapted orbital. By symmetry adapted we mean that the electron orbitals transform according to some irreducible representation of the point group appropriate to the nuclear configuration. One may generate this solution from the Fock operator given in Eq. (4) by use of Lagrange multipliers. Thus one solves

$$F\varphi_a=\sum_{b=1}^{n}\epsilon_{ab}\varphi_b . \tag{6}$$

Here F is still as given in Eq. (4) but the parameters ϵ_{ab} are chosen to satisfy orthonormality of the solutions and to satisfy the symmetry constraint. This level of equation is called the spin-polarized-Hartree-Fock theory (SPHF). Unlike the UHF formalism, chemical bonds may not properly dissociate owing to the constraint on symmetry. However, the SPHF formalism shares one advantage in common to the UHF formalism. That is, when one used Koopman's theorem to construct the ionization energies, one retains information on the multiplet splitting of the resulting ion. We have not tested the SPHF formalism in this study.

The next important level of constraint is to require that all orbitals be symmetry adapted and to require that orbitals be doubly occupied insofar as is possible. That is, electrons are grouped in spin-up, spin-down pairs and the spatial parts of such a spin-up, spin-down pair are identical. This approximation is called the restricted-Hartree-Fock formalism (RHF) and is usually what most authors refer to as Hartree-Fock theory.[1] We note historically, that Wigner,[12] in defining the concept of correlation energy, based his definition on the RHF ground state of a free-electron gas, and thus one may properly think of SPHF or UHF theories as containing correlation insofar as they produce lower total energies than does the RHF wave function. The RHF theory does not permit chemical bonds to properly dissociate, nor does it retain multiplet information when using Koopman's theorem. The orbital equation for the RHF system is formally similar to Eq. (6) with the ϵ_{ab} properly chosen to allow one to satisfy the constraints.

It is possible to remedy some of the defects of the RHF method, or indeed even the UHF method, by constructing a multideterminantal trial wave function. That is, one assumes

$$\Psi(\vec{x}_1\cdots\vec{x}_n)\cong\sum_{\alpha=1}^{\infty}a_\alpha\psi_\alpha(\vec{x}_1\cdots\vec{x}_n) . \tag{7}$$

Here the ψ_α are the Hartree-Fock states, and the a_α are variationally chosen. If the functional forms of the φ's in the ψ_i's are varied along with the a_α, then a multiconfiguration, self-consistent-field solution (MCSCF) is found. We will discuss a particular form of MCSCF theory which is in common use for chemical studies. This method is the general-valence-bond method (GVB) in the perfect-pairing limit.[13] In this model the trial wave function is

$$\Psi(\vec{x}_1\cdots\vec{x}_n)\approx\tilde{A}[\varphi_1\cdots\varphi_{i-1}(\varphi_{ia}^2-c\varphi_{ib}^2)\varphi_{i+1}\cdots\varphi_n] . \tag{8}$$

In Eq. (8) the φ_{ia}^2 indicates a doubly occupied spin orbital. Thus, in the GVB formalism, electrons are correlated in pairs, and any number of pairs may be correlated. Thus, if the pair of electrons in state i is in a chemical bond, the GVB formalism permits proper dissociation of this bond. The noncorrelated orbitals occurring in Eq. (8) are obtained in an RHF form. We shall see from the study on Li that the UHF formalism permits a higher degree of correlation, than does the GVB formalism for some small metal particles.

There seems, to us, to exist substantial differences between small covalent molecules, for which the perfect-pairing GVB method was developed, and even small pseudometallic clusters such as studied here. These differences may be stated qualitatively. In the case of a small covalent molecule one may regard bonding electrons as being localized in bond pairs, and the dominant correlation present as being the dynamic correlation of the pair of electrons in each bond. This limit is well treated in the GVB formalism since the wave function, Eq. (8), for such a pair of electrons contains explicit correlation for this pair. Mathematically speaking one can generate localized solution for electrons in a bond in such systems by rotation in the RHF manifold. In the case of metals or even quasimetals, such localization may not be obtainable. For example in the current case of a nine-atom Li cluster, look at a state $S_z = \frac{1}{2}$. Here, for a cubic cluster in the RHF limit, the ground state is degenerate and one cannot rotate the RHF solution into simple local form without also raising the system energy by promoting the system to an excited state. Furthermore each electron appears to strongly interact dynamically with all others and hence the first electron of the nine valence electrons in Li_9 needs to be correlated with all eight other electrons, and these in turn with all others, so that a simple GVB-pair correlation calculation requires at least 37 configurations to take care of all valence pairs. Furthermore this neglects all three-body or higher correlations which are likely to be important in such a system. Finally each electron participates in more than one bond pair and hence this system is not well described in the simpler GVB formation if at all. The situation for eight-atom Li systems is different. In this case the ground state is nondegenerate and one can easily rotate into a local-bond-type representation, and the GVB formalism is an improvement over UHF (in this case we find the UHF and RHF solutions equivalent at the equilibrium lattice separation). Because of these considerations, we find a UHF formalism preferable to the RHF or GVB perfect-pairing description for general studies of metallic or pseudometallic clusters.

The final approach is the $X\alpha$ method. Since this method has been the subject of numerous recent reviews, we only briefly mention the basic concepts here.[1] This method is an attempt to use the Hohenberg-Kohn theorem. This theorem says the ground-state energy of a nondegenerate Fermi system in a local field is a unique functional of the particle density. That is, if $n(\vec{r})$ is the electron density, one has

$$E_g = E(n(\vec{r})) . \qquad (9)$$

The proper functional $E(n(\vec{r}))$ is not known, in general, but the $X\alpha$ method is one attempt to approximate this functional. The $X\alpha$ functional shares one virtue in common with the UHF method, and this is that chemical bonds properly dissociate in this method. By contrast with the UHF solution, however, the $X\alpha$ solution is not variational, and hence the resultant energy is not an upper bound to the true energy. There is one additional problem in applying the $X\alpha$ method to metals and cluster systems. The Hohenberg-Kohn theorem is only true for systems in their ground state if the system is in a nondegenerate state; therefore, if one studies degenerate systems such as magnetic materials or even certain Li_9 or Li_{13} atom clusters which have degenerate ground states, the energy functional, in Eq. (9), is now a functional of the first-order density matrix, not the particle density and the $X\alpha$ model contains a further and as yet ill-defined approximation.

III. APPLICATION TO LITHIUM CLUSTERS

To test the applicability of the various forms of Hartree-Fock theory and to obtain comparisons with existing $X\alpha$ calculations, we set out to do a series of calculations on eight- and nine-atom clusters of Li. We made preliminary calculations using the RHF, the GVB, and the UHF methods. Initially we attempted a solution to the RHF equation for the Li nine-atom cluster. It was found, when all effects of the RHF constraints were imposed, that the outer valence electrons were unbound. This clearly indicated to us that severe spin polarization was occurring. A next attempt was made to split the pairs of valence electrons by the GVB method. In this calculation, we found that the valence and core electron densities shifted severely with respect to one another, but the energetics were little improved. This result indicated two possibilities. The first is that core polarizations might be important and the second, that correlations beyond simple pair correlation might be important. To remedy these defects most economically, we proceeded to study our system using the UHF method. The UHF solutions to the Li nine-atom cluster exhibited none of the defects of the RHF or GVB solutions. In what follows, we discuss our UHF results for a Li atom, Li_2 molecule, and eight- and nine-atom Li clusters.

Our calculation employed an analytic, Cartesian Gaussian basis. The basis consisted of three s-like contracted orbitals on each Li atom and a polarization p_x, p_y, p_z function. The basis set is given in Table I. The eight-atom cluster geometry chosen was a simple cube, and the length of the cube edge (also here the nearest-neighbor distance) was varied to find a least energy. The eight-atom cluster is found to be bound with a binding energy of 0.008 hartree/atom for a cube edge of 6.15 a u. By means of comparison the UHF, Li_2 molecule has a binding energy of 0.002 hartree/atom and a nearest-neighbor distance of 5.75

TABLE I. Basis set used in these calculations. Only the P_x function is shown here as the P_y and P_z are similar except for the angular part. Each basis function is a sum of Gaussians of the form $x_j(\vec{r}) = F(\theta, \varphi) \sum_i a_j^i N_i e^{-\alpha_i r^2}$. The N_i are chosen to normalize the individual Gaussians and the $F(\theta, \varphi)$ are the angular parts (i.e., s-like, p_x-like, etc.).

Basis function	Symmetry	α_i	a_j^i
1	s	4.0	0.569 22
1	s	0.6	0.583 41
2	s	0.09	1.0
3	s	0.03	1.0
4	P_x	0.08	0.738 88
4	P_x	0.02	0.673 84

a.u. The UHF solution dissociates properly into atoms. The nine-atom cluster was studied in a bcc array and the nearest-neighbor (nn) distance (here the nn distance is $\sqrt{3}/2$ the cube edge) varied to find the minimum energy. The geometries are shown in Fig. 1. The binding energy here is found to be 0.0105 hartree/atom for a nn distance of 5.66 a.u. The one-electron energy levels and the approximate symmetries of the one-electron orbitals are given for the Li atom and for the eight- and nine-atom clusters in Table II. The results of Fripiat *et al.* are also given for comparison. In the case of the eight-atom cluster, the UHF orbitals were exact symmetry orbitals, whereas for the nine-atom cluster the orbitals were not, and only the dominant symmetry component is seen in Table II. In Fig. 2, we show the binding energy versus nn distance for Li_2 and the eight- and nine-atom clusters. In Fig. 3 we show the electronic charge density obtained for both the eight- and nine-atom clusters as a function of position for the line joining the center of the cube to an atom at the cube corner. In the case of the nine-atom cluster we find the density in the interstitial region to be constant 0.008 electrons/a.u.^{3}, whereas for a perfect free-electron gas the density would be 0.007 electron/a.u.^{3} This indicates a migration of the electrons into the sample and hence a "surface dipole layer" is formed here. In Sec. IV we argue that this layer has the proper sign and perhaps a reasonable magnitude.

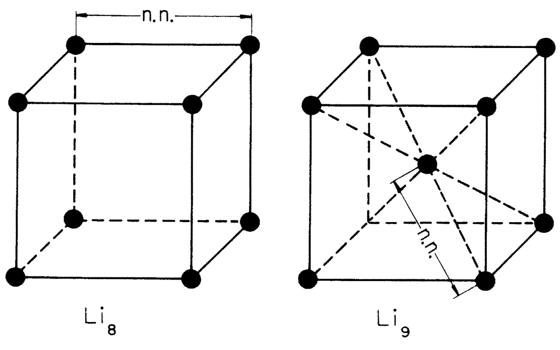

FIG. 1. Geometries of the Li_8 and the Li_9 atom systems are shown.

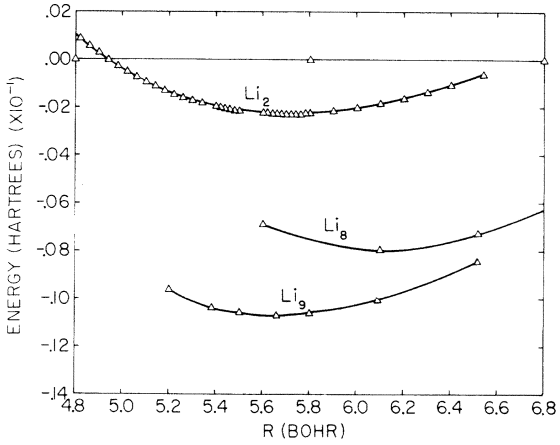

FIG. 2. Binding energy per atom is shown as a function of nearest-neighbor distance for Li_2 and the eight- and nine-atom Li systems. Results in a.u.

IV. DISCUSSION OF RESULTS AND CONCLUSIONS

The authors are not aware of any direct evidence for the properties of fine particles of lithium. However we do know some limiting behavior. That is, the lithium-atom properties and the properties of bulk metallic lithium are well known. In Table III we summarize some known experimental evidence for Li and also give a summary of cluster results using our UHF calculations. By way of comparison we also quote the cluster results obtained by Fripiat *et al.*, using

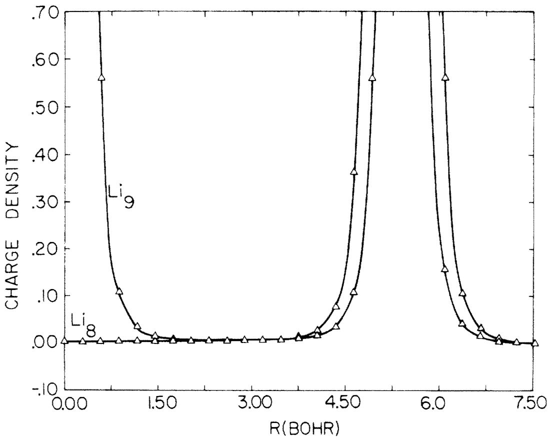

FIG. 3. Charge density for Li_8 and Li_9 for the line joining the center of the cube to an atom on the cube corner is shown. The plots are for the equilibrium geometry and results are in a.u.

TABLE II. Valence-electron energies for the various size Li clusters. The UHF values are from the present calculation and the $X\alpha$ values are from Ref. 6. Results are in eV.

Li_8 UHF		Li_8 $X\alpha$		Li_9 UHF		Li_9 $X\alpha$	
Energy	Spin type and approx. symmetry	Energy	Spin type and symmetry	Energy	Spin type and approx. symmetry	Energy	Spin type and symmetry
−7.59	a_{1g} α	−5.4	a_{1g} α	−6.97	a_{1g} α	−5.6	a_{1g} α
−4.54	t_{1u} α	−3.8	t_{1u} α	−5.06	t_{1u} α	−4.1	t_{1u} α
−4.54	t_{1u} α	−3.8	t_{1u} α	−4.96	t_{1u} α	−4.1	t_{1u} α
−4.54	t_{1u} α	−3.8	t_{1u} α	−4.87	t_{1u} α	−4.1	t_{1u} α
−7.59	a_{1g} β	−5.4	a_{1g} β	−3.41	e_g α	−2.7	e_g α
−4.54	t_{1u} β	−3.8	t_{1u} β	−7.72	a_{1g} β	−5.0	a_{1g} β
−4.54	t_{1u} β	−3.8	t_{1u} β	−5.22	t_{1u} β	−3.8	t_{1u} β
−4.54	t_{1u} β	−3.8	t_{1u} β	−5.13	t_{1u} β	−3.8	t_{1u} β
				−4.67	t_{1u} β	−3.8	t_{1u} β

the $X\alpha$ method.[6] The experimental data are obtained from standard sources.[14] We note that the properties of other small particles of metals such as Be are known and that the available evidence tends to suggest that experimental quantities such as the work function tend to the bulk value by the time the cluster size is about 10–15 Å in size.[8]

One may draw some immediate conclusions from Table III. The UHF results for binding energy per atom are a great underestimation, whereas the geometric trends seem reasonably accurate. This binding-energy error for Li is expected to be due to the ignoring of configuration interaction in the UHF calculation, and the good geometric information is also normal to UHF- or RHF-type calculations. We note the trend of the binding energy per atom to increase monotonically toward the solid-state value for the UHF case, but not for the $X\alpha$ case. This effect may be due to the fact that the $X\alpha$ spin orbitals are symmetry adapted but the UHF orbitals are not. Thus, in the $X\alpha$ nine-atom cluster, the state computed is a state which is degenerate. By the Jahn-Teller theorem the stable state must be nondegenerate.[15] Therefore the nine-atom cluster must distort to remove the degeneracy, and the $X\alpha$ nine-atom cluster can-

TABLE III. Values of several experimental quantities are given for Li, Li_2, and Li metal and also for eight, nine, -13-atom clusters. The UHF values are from the current calculation. The $X\alpha$ results are from Ref. 6 and the experimental data are from Ref. 14. In these tables energies are in eV, lengths in a.u. (1 a.u. ≈ 0.53 Å), ϵ_f is the Fermi energy, ϵ_w is the work function or ionization energy, nn is the nearest-neighbor distance, and E_b the binding energy per atom. In the case of ϵ_w, the values are from transition-state calculations for the $X\alpha$ system, with the $X\alpha$ eigenvalues given in parentheses as a means of comparison.

Property / Calc. / System	ϵ_f			ϵ_w			nn			E_b		
	Expt.	UHF	$X\alpha$	Expt.	UHF	$X\alpha$	Expt.	UHF	$X\alpha$	Expt.	UHF	$X\alpha$
Li atom	···	···	···	5.39	5.34	5.4 (2.6)	···	···	···	0	0	0
Li_2	···	···	···		4.71	5.2 (3.2)	5.04	5.60	5.08	0.52	0.03	0.40
Li_8	···	2.67	1.4[b]	···	4.36	4.8 (3.8)	···	6.08	5.59	···	0.11	0.78
Li_9	···	4.31	2.8[b]	···	3.41	3.9 (2.7)	···	5.66	5.25	···	0.15	0.74
Li_{13}(icos)	···	···	2.8[b]	···	···	4.3 (3.7)	···	···	6.10	···	···	0.97
Li metal	3.0	7.2[a]	···	2.28		···	5.65	···	···	1.50	···	···

[a] This value is an RHF bulk-crystal value obtained by Monkherst. Appropriate correlation corrections reduce this by some 4 or 5 eV.

[b] These values are obtained using the $X\alpha$ eigenvalues which normally seem to provide adequate information for state densities although the more rigorous transition-state values are needed to provide accurate absolute binding energies.

not be in the lowest energy state. We also note a similar comment applies to the 13-atom cuboctahedral $X\alpha$ cluster, which must also Jahn-Teller distort, whereas the 13-atom orthorhombic cluster ground state is nondegenerate and acceptable. This implies that the $X\alpha$ conclusions regarding the relative binding of eight- and nine-atom clusters are not necessarily correct, and also that the favoring of orthorhombic over a distorted-cubic-type symmetry for the 13-atom cluster clearly needs further study. The UHF case, owing to the absence of symmetry-adapted orbitals, does not have a degenerate ground state for the nine-atom cluster, although our orbital densities indicate a distorted cubic structure to D_{2h} symmetry is preferred. We find the nine-atom cluster better bound than the eight-atom in terms of binding per atom.

The other relevant parameters are the values for the work function and the width of the valence band (Fermi energy). In the UHF case one sees in Table III that all these quantities progress monotonically from the atomic value toward the bulk value with increasing cluster size.

The question of the trend of the work function is significant, we believe, if one is going to use cluster models for studies of catalysis. The work function is determined by two quantities. The first is the band energy for the infinite crystal, assuming the surface at infinity has no dipole moment associated with it, plus the contribution to the surface-dipole layer. We believe that both UHF plus correlation corrections (the correction for the Li Fermi surface is very small compared to other effects here[16]) and $X\alpha$ produce realistic bands for Li. Therefore we conclude that the UHF method produces a surface dipole moment of correct sign and likely the correct magnitude. We think, if one is to understand binding of molecules to surfaces, it is important to first obtain a surface with a reasonable surface-dipole layer. In this regard we believe the UHF method has great promise for such studies. With regard to binding energies, we note that the good values for the $X\alpha$ may be fortuitous since the $X\alpha$ method is not variational, and that an exact $X\alpha$ solution to H_2 overestimates the binding energy by a factor of 2.[17]

ACKNOWLEDGMENTS

The authors greatly appreciate helpful discussions with Dr. S. C. Jain on the subject of properties of small metal clusters, and with Dr. W. Kohn on his recent local-density-approximation studies. The support of the NSF and the U. S. Air Force, Aerospace Laboratory, is greatly appreciated.

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*Work supported in part by the National Science Foundation under Grant DMR-72-03026, and the U. S. Air Force, Aerospace Research Laboratory, Contract F-33615-72-C-1506.

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